



Cavity-Bias Sampling in Reaction Ensemble Monte Carlo Simulations

by J. K. Brennan

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Cavity-bias sampling in reaction ensemble Monte Carlo simulations

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A methodology is presented to sample efficiently configurations of reacting mixtures in the reaction ensemble Monte Carlo simulation technique. A cavity-biasing scheme is used, which more effectively samples configurations than conventional random sampling. Akin to other biasing schemes that are implemented into insertion-based Monte Carlo methods such as Gibbs ensemble Monte Carlo, the method presented here searches for space in the reacting mixture whereby the insertion of a product molecule is energetically favoured. This sampling bias is then corrected in the acceptance criteria. The approach allows for the study of reacting mixtures at high density as well as for polyatomic molecular species. For some cases, the method is shown to increase the efficiency of the reaction steps by a factor greater than 20. The approach is shown to be readily generalized to other biasing schemes such as orientational-biasing of polar molecules and configurational-biasing of chain-like molecules.

1. Introduction

The reaction ensemble Monte Carlo simulation method (RxMC) is a powerful simulation tool for studying the behaviour of chemical reaction equilibria [1, 2]. The RxMC technique can be used to predict the shift in reaction equilibria for an ideal-gas phase reaction in a non-ideal environment such as a condensed phase, a solvent, or a porous material. Recent applications of the RxMC method include reactions of plasmas [3], reactions in porous carbons [4–7] and porous membranes [8], reactions under shock conditions [9], and reactions in supercritical fluid solvents [10, 11]. Comprehensive reviews of the RxMC method [12] and its applications to date [13] can be found elsewhere.

As part of the configuration sampling algorithm in the RxMC method, the insertion and deletion of molecules is required to satisfy the reaction equilibrium condition $\sum_{i=1}^C v_{ji} \mu_i = 0$, where v_{ji} is the stoichiometric coefficient of species i in chemical reaction j , μ_i is the chemical potential of species i in the reacting mixture, and C is the total number of reactants and products. Analogous to other Monte Carlo (MC) methods such as grand canonical ensemble MC (GCMC) [14, 15] and Gibbs ensemble MC (GEMC) [16, 17] that require the insertion

of molecules into the simulation box, random insertion fails for high density systems or for multi-site models such as polymers in even moderately dense systems. Conventional random sampling fails due to the high probability of the inserted molecule encountering an overlap with molecules already in the simulation box, generating a configuration that is energetically unfavorable and most probably rejected.

Previous applications of the RxMC method successfully used conventional random sampling because low density phases were studied or simple molecular models were considered. In this work, we present a cavity-bias sampling method for the RxMC technique that makes it possible to simulate reaction equilibria at conditions where conventional sampling fails. The method, termed cavity-bias reaction ensemble Monte Carlo (CB-RxMC) is analogous to bias sampling schemes used in the GCMC [18, 19] and GEMC simulation methods [20]. As the name implies, the method searches for cavities in the system into which product molecules can be successfully inserted. The method can be easily generalized to include other biasing methods such as orientational-biasing and configurational-biasing.

In the following, we briefly review the essentials of the RxMC method, after which we present the formalism of our cavity-bias sampling method for the RxMC technique. We present an example of the method to demonstrate its efficiency.

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2. Formalism

2.1. Reaction ensemble Monte Carlo

The RxMC method is designed to minimize the Gibbs free energy thus determining the true chemical equilibrium state irrespective of rate limitations. RxMC requires intermolecular potentials for the molecular species that are present in the reacting mixture. RxMC also requires inputting the ideal-gas internal modes for each reacting species, information which is readily available in standard sources [21, 22] or can be generated using quantum mechanics methods. Finally, the particular reactions occurring in the system must be specified.

Implementation of RxMC provides information about the chemical equilibrium state, such as the density of the reacting mixture, mole fractions of the reacting species, the change in the total number of moles, and the internal energy. RxMC can be performed in many different types of ensembles [12], including canonical, isothermal–isobaric, Gibbs and other less common ensembles [23]. Furthermore, RxMC can be performed for multiple reactions and multiple phases [24]. RxMC does not simulate bond breaking or formation; rather, RxMC directly samples forward and reverse reaction steps as Monte Carlo-type moves according to the stoichiometry of the reactions being considered.

The isothermal–isobaric ensemble version of the RxMC method for a set of linearly independent chemical reactions involves the following trial moves:

- (1) a change in the position or orientation of a molecule which is chosen at random;
- (2) a random change in the simulation box volume; and
- (3) for a randomly chosen reaction and randomly chosen reaction direction (forward or reverse), reactant molecules are randomly chosen and deleted while product molecules either replace reactant molecules or are inserted randomly into the simulation box.

Step (1) ensures that thermal equilibrium is established for the specified temperature, Step (2) ensures that mechanical equilibrium is established for the specified pressure, and Step (3) ensures that chemical equilibrium is established for the specified reactions.

Step (3) requires the insertion of product molecules into the simulation box. For reactions where the number of moles decreases or remains unchanged, the product molecules can simply be placed in the space previously occupied by the deleted reactant molecules. For reactions where the number of moles increases, some of the product molecules can replace reactant molecules but the remaining product molecules must be inserted into the simulation box. In the conventional sampling

scheme this entails randomly choosing a position in the box. For medium to high density systems, this step can result in a prohibitively low acceptance rate since a random insertion will almost always result in an overlap with molecules already in the box. Such an overlap is energetically unfavourable and therefore the attempted reaction step will nearly always be rejected. Below we describe an algorithm that allows us to bias the insertion of product molecules in such a way that cavities in the system are found. This method of insertion would bias the simulations if the ordinary acceptance rules were used. Therefore, we next demonstrate that the correct distribution of configurations can be sampled if the acceptance rule for this step is modified appropriately.

2.2. General approach for bias Monte Carlo sampling

For completeness, we first consider the general approach for bias Monte Carlo sampling (see [25] for a more thorough account). Let $K(o \rightarrow n)$ be the flow of configuration $o \rightarrow n$, where

$$K(o \rightarrow n) = N(o) \times \alpha(o \rightarrow n) \times acc(o \rightarrow n). \quad (1)$$

$N(o)$ is the probability of being in configuration o ; $\alpha(o \rightarrow n)$ is the probability of generating configuration n ; and $acc(o \rightarrow n)$ is the probability of accepting the move from $o \rightarrow n$. N , often referred to as the probability density or distribution of configurations, depends on the details of the ensemble and can be determined from the partition function. For example, the probability of finding configuration \mathbf{r}^N in the canonical ensemble is

$$N(\mathbf{r}^N) = \frac{\exp[-\beta U(\mathbf{r}^N)]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]} \quad (2)$$

where $U(\mathbf{r}^N)$ is the configurational energy of N particles and $\beta = 1/k_B T$ (k_B is the Boltzmann constant and T is the temperature).

To guarantee a correct sampling scheme, the *detailed balance condition* is imposed

$$K(o \rightarrow n) = K(n \rightarrow o) \quad (3)$$

or more specifically

$$\begin{aligned} N(o) \times \alpha(o \rightarrow n) \times acc(o \rightarrow n) \\ = N(n) \times \alpha(n \rightarrow o) \times acc(n \rightarrow o). \end{aligned} \quad (4)$$

In the original Metropolis scheme, α is chosen to be a symmetric matrix, i.e. $\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$. For a biased Monte Carlo algorithm, we wish to generate configurations in a biasing manner thus making $\alpha(o \rightarrow n) \neq \alpha(n \rightarrow o)$. It is clear from equation (4), that since $\alpha(o \rightarrow n) \neq \alpha(n \rightarrow o)$ and $N(o)$ and $N(n)$ are predetermined we must correct for biasing α by changing the ratio $acc(o \rightarrow n)/acc(n \rightarrow o)$.

Suppose that we have developed a Monte Carlo scheme to generate trial configurations with a probability that depends on the potential energy of that configuration

$$\alpha(o \rightarrow n) = f[U(n)] \quad (5)$$

and while for the reverse move

$$\alpha(n \rightarrow o) = f[U(o)]. \quad (6)$$

From equation (4) then

$$\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \frac{f[U(o)] N(n)}{f[U(n)] N(o)}. \quad (7)$$

A possible acceptance rule that obeys this condition is

$$acc(o \rightarrow n) = \min\left(1, \frac{f[U(o)] N(n)}{f[U(n)] N(o)}\right). \quad (8)$$

It is clear then that we can introduce an arbitrary biasing function $f[U]$ in the sampling scheme, provided that the acceptance rule is modified in such a way that the bias is removed [25]. Note that the same biasing function must be used to generate the o configurations and the n configurations.

2.3. Derivation of acceptance rule for CB-RxMC

For a reaction step in RxMC, the ratio of the probability densities of the old ' o ' and the new ' n ' configurations can be written

$$\frac{N(n)}{N(o)} = \prod_{i=1}^{c_j} \frac{N_i!}{(N_i + v_{ji}\xi_j)!} \left(\frac{q_{\text{int},i} V}{\Lambda_i^3} \right)^{v_{ji}\xi_j} \times \exp[-\beta(U_i(n) - U_i(o))] \quad (9)$$

where c_j is the total number of species in reaction j ; N_i is the total number of molecules of species i ; v_{ji} is the stoichiometric coefficient of species i in reaction j ; ξ_j is the molecular extent of reaction for reaction j ;

$q_{\text{int},i}$ is the quantum partition function for the internal modes of an isolated molecule of species i , which includes vibrational, rotational, and electronic; Λ_i is the thermal de Broglie wavelength of species i ; and V is the total volume of the system [1, 2]. Equation (9) is appropriate for both forward and reverse reaction steps ($\xi_j = 1$ for a forward step and $\xi_j = -1$ for a reverse step), where the stoichiometric coefficients are taken to be positive for product species and negative for reactant species. U_i is the configurational energy between molecule i and all other molecules in the simulation box, so for a deleted reactant molecule $U_i(n) = 0$, while for an inserted product molecule $U_i(o) = 0$. From equation (9) we can write the acceptance rule for a reaction step using conventional sampling in RxMC as

$$acc(o \rightarrow n) = \min\left[1, \prod_{i=1}^{c_j} \left[\frac{N_i!}{(N_i + v_{ji}\xi_j)!} \left(\frac{q_{\text{int},i} V}{\Lambda_i^3} \right)^{v_{ji}\xi_j} \times \exp[-\beta(U_i(n) - U_i(o))] \right] \right]. \quad (10)$$

Similar to other biasing algorithms [25], we can define a Rosenbluth factor

$$W_i(n) = \sum_{l=1}^{k_i} \exp[-\beta U_i(l)], \quad (11)$$

which, for a single attempted move, is determined by generating k_i trial configurations for species i , i.e. when i is a reactant molecule k_i trial deletions and when i is a product molecule k_i trial insertions. From these trial configurations we can select a configuration, m , for species i with a probability

$$f(U_i) = \frac{\exp[-\beta U_i(m)]}{\sum_{l=1}^{k_i} \exp[-\beta U_i(l)]} \quad (12)$$

where $f(U_i)$ is a biasing function that ensures energetically favourable configurations are generated. The expression for the complete reaction step is then

$$f[U(o)] = \prod_{i=1}^{c_j} f[U_i(o)] = \prod_{i=1}^{c_j} \frac{\exp[-\beta U_i(o)]}{\sum_{l=1}^{k_i} \exp[-\beta U_i^o(l)]} \quad (13)$$

where we can write an analogous expression for $f[U(n)]$.

Substituting expressions for $f[U(o)]$, $f[U(n)]$ and equation (9) into equation (7) we get the probability

of accepting the reaction step attempt as

$$\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \prod_{i=1}^{c_j} \left[\frac{N_i!}{(N_i + v_{ji}\xi_j)!} \left(\frac{q_{\text{int},i} V}{\Lambda_i^3} \right)^{v_{ji}\xi_j} \exp[-\beta(U_i(n) - U_i(o))] \right. \\ \left. \times \frac{\exp[-\beta U_i(o)]}{\sum_{l=1}^{k_i} \exp[-\beta U_i^o(l)]} \frac{\sum_{l=1}^{k_i} \exp[-\beta U_i^n(l)]}{\exp[-\beta U_i(n)]} \right] \quad (14)$$

while after simplifying we get

$$\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \prod_{i=1}^{c_j} \left[\frac{N_i!}{(N_i + v_{ji}\xi_j)!} \left(\frac{q_{\text{int},i} V}{\Lambda_i^3} \right)^{v_{ji}\xi_j} \frac{\sum_{l=1}^{k_i} \exp[-\beta U_i^n(l)]}{\sum_{l=1}^{k_i} \exp[-\beta U_i^o(l)]} \right]. \quad (15)$$

Finally then, the acceptance rule for a reaction step that satisfies the detailed balance condition is

$$acc(o \rightarrow n) = \min \left[1, \prod_{i=1}^{c_j} \left[\frac{N_i!}{(N_i + v_{ji}\xi_j)!} \left(\frac{q_{\text{int},i} V}{\Lambda_i^3} \right)^{v_{ji}\xi_j} \times \frac{\sum_{l=1}^{k_i} \exp[-\beta U_i^n(l)]}{\sum_{l=1}^{k_i} \exp[-\beta U_i^o(l)]} \right] \right]. \quad (16)$$

Recall that when i is a deleted reactant molecule, $U_i^n(l) = 0$ for all l s, so $\sum_{l=1}^{k_i} \exp[-\beta U_i^n(l)] = k_i$. Likewise, when i is an inserted product molecule, $U_i^o(l) = 0$ for all l s, so $\sum_{l=1}^{k_i} \exp[-\beta U_i^o(l)] = k_i$. Finally, note that when $k_i = 1$ for all species, equation (16) reduces to the conventional sampling acceptance rule given in equation (10).

With minor extensions, the above scheme can be applied to include orientational-biasing algorithms for molecular models with a strong dependence on relative orientation (e.g. polar and hydrogen-bonded molecules and multi-atomic models) or configurational-biasing schemes for chain-like molecules [25]. Using the Rosenbluth factors, equation (15) can be generalized to accommodate such biasing schemes by writing

$$\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \prod_{i=1}^{c_j} \left[\frac{N_i!}{(N_i + v_{ji}\xi_j)!} \left(\frac{q_{\text{int},i} V}{\Lambda_i^3} \right)^{v_{ji}\xi_j} \frac{W_i(n)}{W_i(o)} \right]. \quad (17)$$

Appropriate evaluation of the Rosenbluth factors for the particular scheme is required.

2.4. CB-RxMC algorithm

Next, we provide a detailed outline for implementing the CB-RxMC algorithm. For simplicity, consider a system of J reactions where all reacting species are modelled as single spheres and electrostatic contributions are ignored. (Again, this algorithm can be readily extended to include multi-atomic and electrostatic molecular models.)

- Step 1: Randomly choose reaction j and the reaction direction (forward or reverse).
- Step 2: Randomly select reactant molecules and determine $\exp[-\beta U_i^o(1)]$ for each of these reactant molecules, where $l = 1$.
- Step 3: For each reactant molecule, generate $k_i - 1$ trial configurations denoted $b_2 \dots b_{k_i}$ and determine $\sum_{l=2}^{k_i} \exp[-\beta U_i^o(b_l)]$. Note that for reactants whose centre-of-mass will be replaced by the centre-of-mass of a product molecule, $k_i = 1$.
- Step 4: For product molecules whose centre-of-mass will replace the centre-of-mass of a deleted reactant molecule, determine $\exp[-\beta U_i^n(1)]$ where $l = 1$, and set $k_i = 1$.
- Step 5: For the remaining product molecules that need to be inserted for reaction j , generate k_i trial configurations, denoted $b_1 \dots b_{k_i}$, by randomly inserting the product molecule into the simulation box and determine $\sum_{l=1}^{k_i} \exp[-\beta U_i^n(b_l)]$. From these k_i insertions, select one with the probability given in equation (12).
- Step 6: The attempted reaction step for reaction j is accepted with the probability given in equation (16).

It is implicitly assumed that when product molecules are inserted they are placed in the locations previously occupied by reactant molecules. This is not a requirement of the RxMC method but for most cases will enhance the phase sampling efficiency. Moreover, replacing reactant molecules with product molecules which have similar molecular model character (e.g. size, atomistic detail, or polarity) will further increase sampling efficiency. However, the reactant-to-product replacement must be consistent for the forward and reverse directions for a particular reaction throughout the simulation run. For example, if a type a molecule is replaced by a type b molecule in the forward direction of a reaction step, then a type b molecule must be replaced by a type a molecule in the reverse direction [1, 2].

An alternative but less efficient approach (for most cases) would be to randomly insert all product molecules. The necessary minor adjustments to the above algorithm would be to ignore the last sentence in Step 3 and to remove Step 4. Finally, additional trial insertions could be attempted beyond simply replacing a reactant molecule with a product molecule. This may improve the acceptance rate in cases where the molecular model character of the corresponding product and reactant are markedly dissimilar. If additional trial insertions are attempted, then $k_i \neq 1$ in Steps 3 and 4.

2.5. Choice of k_i

The efficiency of the CB-RxMC algorithm depends on the choice of k_i , the number of trial insertions for a given product molecule. In principle, k_i can be chosen without restrictions; however, there is a computational expense to be paid for increasing the number of attempted insertions. The optimal choice of k_i will allow for sampling of a wide portion of phase space but in a cost effective manner. A straightforward approach for selecting k_i is to adjust its value based on a desired acceptance ratio for each reaction. k_i could then be adjusted automatically during the simulation, analogous to the adjustments which are typically made to the maximum allowable changes for particle displacements and volume changes [25, 26]. For some systems, however, as k_i is increased, eventually the computational cost of additional trial insertions will outweigh the benefits of an increased acceptance ratio. In the following, we propose some simple guidelines for optimizing the CB-RxMC algorithm with respect to k_i . The approach is based on previous work that optimized a configurational-bias Monte Carlo method applied to chain molecules [27].

We approximate the efficiency of the CB-RxMC scheme to be: (a) proportional to the probability that a given trial configuration is successfully generated; and (b) inversely proportional to the computational cost of generating a configuration. We can write then that

$$\text{Efficiency} = \frac{\langle \text{acceptance} \rangle}{\langle \text{cost} \rangle} \quad (18)$$

where $\langle \text{acceptance} \rangle$ is the average acceptance ratio defined as the number of accepted reaction steps over the number of attempted reaction steps for the entire simulation run, while $\langle \text{cost} \rangle$ is the average computational cost of generating an attempted reaction. In practice, a series of short simulations can be performed for various k_i 's to determine the *Efficiency* as a function of k_i . The maximum in the *Efficiency* vs. k_i plot will then provide the optimal value for k_i . As the number

of trial insertions increases, the value of $\langle \text{cost} \rangle$ rises. From equation (18), we expect that for systems where the probability of successful insertions will be high, e.g. low density systems, the optimal value of k_i will increase monotonically with increasing k_i . However for high density systems in which $\langle \text{acceptance} \rangle$ marginally increases with k_i , the optimal value of k_i will shift to lower values.

Note that for multiple reaction systems the value of k_i is not required to be the same for all reactions, but it does need to be the same for each reactant-to-product replacement pair for a particular reaction. Also, the choice of k_i will strongly depend on the state point considered as well as the details of the molecular models. Typical values of k_i range from 2–200 attempted insertions since reaction acceptance ratios can vary widely.

3. Application

We illustrate the method using the reacting system, $2\text{H}_2\text{O} + \text{C}_2\text{H}_4 \rightleftharpoons 2\text{CO} + 4\text{H}_2$. The forward reaction requires the insertion of three product molecules into the simulation box and therefore provides a stringent test for the CB-RxMC algorithm.

3.1. Molecular models and computational details

The molecular species C_2H_4 , CO , and H_2 are modelled as single spherical particles interacting through the exponential-6 potential where electrostatic contributions are ignored [28]. The water model consists of an exponential-6 group at the oxygen centre and a set of three fixed-point charges [29].

Unlike interactions between species are approximated by the Lorentz–Berthelot mixing rules [30]. A spherical cutoff of 1.05 nm was applied for the particle–particle interactions with standard corrections for this truncation added [26]. Long-range electrostatic interactions were determined by using the Ewald summation method [26]. Applying a prescription for optimizing the Ewald parameters [31, 32] led to approximately 1000–1200 wave vectors used in the k-space sum where the same truncation distance as above was applied for the real space sum. The ideal-gas partition functions for H_2O , C_2H_4 , CO , and H_2 that are required in the RxMC method were taken from standard thermochemical reference data [22].

Simulations were performed in steps, where a step (chosen with equal probability) was either a molecule displacement and rotation (for H_2O molecules only), a forward reaction step, or a reverse reaction step. A change in the simulation cell volume was attempted every 3000 steps. The maximum allowable changes for

the displacement, rotation, and volume change steps were all adjusted to achieve an acceptance fraction of 0.4. Simulations were equilibrated for $2\text{--}3 \times 10^6$ steps after which averages of the desired quantities were taken over 5×10^6 steps. Reported uncertainties were estimated using the method of block averages [25].

3.2. Results

A series of constant-pressure RxMC simulations for the $2\text{H}_2\text{O} + \text{C}_2\text{H}_4 \rightleftharpoons 2\text{CO} + 4\text{H}_2$ reaction were performed at a temperature of 900 K. The initial configuration for each simulation was 250 H_2O molecules and 350 C_2H_4 molecules placed randomly on a face-centred-cubic lattice. Several pressures were considered (100, 300 and 500 MPa) that span a range of densities. Further, a wide range of k_i values were considered: 1, 5, 10, 20, 40, 80, and 120. Simulations where $k_i = 1$, represent conventional sampling of reactions steps in the RxMC method.

CB-RxMC simulation results are presented in table 1. The average configurational energy, U , and specific volume, v , are reported along with the average

number of molecules for each species, N_i . As expected, for all values of k_i the calculated quantities are within estimated uncertainties. Effects of increasing k_i can be seen by considering the changes in the acceptance ratio which is also reported in table 1. The definition of the acceptance ratio is the same as that used in equation (18). (Note that at equilibrium the forward and reverse reaction acceptance ratios will be equal, therefore only one value is reported.) Table 1 shows that as the number of trial insertions increases, the acceptance ratio also increases. The acceptance ratios for the three pressures considered improve by factors of about 3, 11 and 23, respectively.

Next, we can determine an estimate for the optimal value of k_i using the guidelines presented in section 2.5. In order to dimensionalize $\langle \text{cost} \rangle$ in equation (18), we have introduced a unit of computational cost to be the time needed to compute equation (16) when $k_i = 1$ for all species. A plot of the *Efficiency* as a function of k_i is given in figure 1, where the plotted values are also given in table 2. Ensemble averages of $\langle \text{acceptance} \rangle$ and $\langle \text{cost} \rangle$ were determined from the entire simulation run. All

Table 1. CB-RxMC simulation results for the $2\text{H}_2\text{O} + \text{C}_2\text{H}_4 \rightleftharpoons 2\text{CO} + 4\text{H}_2$ reaction.^a

k_i	U [kJ/mol]	v [cm ³ /g]	N_i^b				Acceptance ratio
			H ₂ O	CO	H ₂	C ₂ H ₄	
$P = 100$ MPa							
1	−2.930 (0.031)	4.428 (0.011)	201.3 (0.3)	48.7 (0.3)	96.5 (0.6)	325.7 (0.2)	0.1329
5	−2.929 (0.032)	4.422 (0.017)	201.2 (0.2)	48.7 (0.2)	97.5 (0.5)	325.6 (0.1)	0.3445
10	−2.937 (0.023)	4.427 (0.015)	201.3 (0.1)	48.7 (0.2)	97.3 (0.3)	325.7 (0.1)	0.3718
20	−2.930 (0.035)	4.426 (0.014)	201.3 (0.3)	48.7 (0.3)	97.4 (0.5)	325.6 (0.1)	0.3870
40	−2.950 (0.033)	4.422 (0.018)	201.4 (0.3)	48.6 (0.3)	97.1 (0.5)	325.7 (0.1)	0.3939
80	−2.933 (0.039)	4.423 (0.020)	201.3 (0.3)	48.7 (0.3)	97.4 (0.6)	325.7 (0.2)	0.3989
120	−2.922 (0.031)	4.429 (0.016)	201.3 (0.2)	48.7 (0.2)	97.4 (0.5)	325.6 (0.1)	0.4017
$P = 300$ MPa							
1	−6.526 (0.128)	2.169 (0.006)	232.2 (0.3)	17.7 (0.3)	34.5 (0.6)	341.2 (0.2)	0.0141
5	−6.713 (0.147)	2.157 (0.012)	232.6 (0.3)	17.4 (0.3)	34.7 (0.5)	341.3 (0.1)	0.0844
10	−6.494 (0.117)	2.170 (0.008)	232.3 (0.3)	17.7 (0.3)	35.5 (0.5)	341.1 (0.1)	0.1212
20	−6.553 (0.127)	2.167 (0.008)	232.3 (0.3)	17.7 (0.3)	35.3 (0.6)	341.2 (0.2)	0.1361
40	−6.518 (0.110)	2.169 (0.007)	232.3 (0.3)	17.7 (0.3)	35.4 (0.6)	341.1 (0.2)	0.1461
80	−6.487 (0.084)	2.170 (0.005)	232.2 (0.2)	17.8 (0.2)	35.5 (0.4)	341.1 (0.1)	0.1508
120	−6.368 (0.130)	2.176 (0.008)	231.9 (0.4)	18.1 (0.3)	35.1 (0.5)	341.0 (0.1)	0.1565
$P = 500$ MPa							
1	−7.819 (0.089)	1.755 (0.005)	239.5 (0.3)	10.5 (0.3)	20.9 (0.5)	344.7 (0.1)	0.0037
5	−8.024 (0.242)	1.746 (0.006)	239.9 (0.2)	10.2 (0.2)	20.4 (0.5)	344.9 (0.1)	0.0321
10	−7.818 (0.142)	1.753 (0.003)	239.5 (0.2)	10.4 (0.2)	20.9 (0.4)	344.8 (0.1)	0.0549
20	−7.758 (0.080)	1.756 (0.003)	239.5 (0.2)	10.5 (0.2)	21.0 (0.3)	344.7 (0.1)	0.0707
40	−7.742 (0.130)	1.757 (0.005)	239.4 (0.2)	10.6 (0.2)	21.1 (0.3)	344.7 (0.1)	0.0814
80	−7.834 (0.129)	1.756 (0.005)	239.5 (0.2)	10.5 (0.2)	21.0 (0.4)	344.8 (0.1)	0.0844
120	−7.859 (0.117)	1.753 (0.004)	239.5 (0.2)	10.5 (0.2)	20.9 (0.3)	344.8 (0.1)	0.0852

^aUncertainty in units of the last decimal digit is given in parentheses: −2.930 (0.031) implies -2.930 ± 0.031 .

^bNumber of molecules of species *i*.

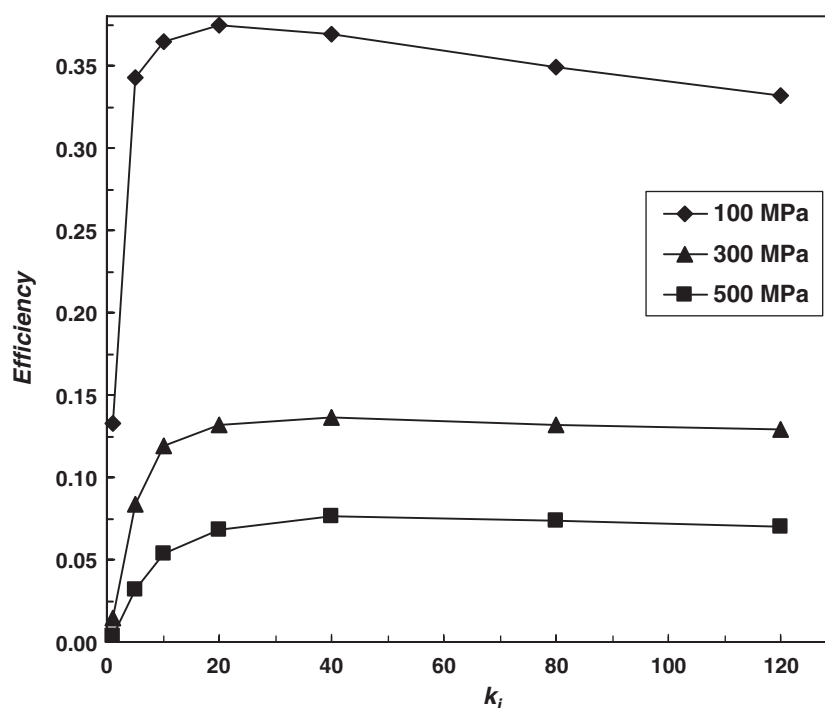


Figure 1. Efficiency of the CB-RxMC algorithm as a function of the number of trial insertions for the $2\text{H}_2\text{O} + \text{C}_2\text{H}_4 \rightleftharpoons 2\text{CO} + 4\text{H}_2$ reaction at the three pressures considered. Line is shown as a guide to the eye only.

Table 2. Efficiency at various k_i values for the $2\text{H}_2\text{O} + \text{C}_2\text{H}_4 \rightleftharpoons 2\text{CO} + 4\text{H}_2$ reaction.

k_i	Efficiency ^a		
	100 MPa	300 MPa	500 MPa
1	0.133	0.014	0.0037
5	0.343	0.084	0.0319
10	0.364	0.119	0.0538
20	0.375	0.132	0.0684
40	0.369	0.137	0.0762
80	0.349	0.132	0.0739
120	0.332	0.129	0.0704

^aEfficiency determined from equation (18).

three curves exhibit similar behaviour although the behaviour is most pronounced for the 100 MPa case. Comparing the three curves, for all values of k_i the efficiency decreases as the pressure (and corresponding density) of the system increases. This is expected since the space available for product molecule insertion is also reduced with increasing pressure. The maximum for the 100 MPa system is at approximately $k_i=20$, while the maximum for the 300 and 500 MPa systems is at approximately $k_i=40$. However, significant gains in the efficiency of the CB-RxMC algorithm are found for rather small values of k_i just beyond conventional sampling ($k_i=1$), i.e. $k_i=5, 10$. Beyond the maximum

values of k_i for each pressure considered, the efficiency begins to decrease. This can more clearly be seen by considering table 2. For the 300 and 500 MPa cases it is evident that attempting more than 40 trial insertions per reaction step is not beneficial. Moreover, given the flatness of the curves at high k_i as well as the steep rise at low k_i , the most practical value for k_i is approximately 15–20 trial insertions per attempted reaction. For the 100 MPa case, the optimal value of k_i is more obvious, i.e. $k_i=20$.

4. Conclusions

A cavity-bias algorithm was presented that increases the acceptance rate of reaction steps in the reaction ensemble Monte Carlo method. For some cases, the CB-RxMC method is shown to increase acceptance rates for the reaction step by a factor greater than 20. CB-RxMC enhances phase space sampling but more critically allows for the simulation of systems not feasible with conventional random sampling. CB-RxMC is an extension of other cavity-bias sampling techniques used in the grand canonical ensemble MC method [18]. The main bottleneck of an RxMC simulation is the insertion of product molecules into the simulation box during a reaction step. In a biased fashion, the CB-RxMC method generates energetically favourable

positions for these molecules by searching for cavities in the system. The bias introduced when generating positions is then corrected for in the acceptance criteria. For a given state point, the efficiency of the CB-RxMC technique depends on the number of trial insertions (k_i) for each attempted reaction step. A tradeoff exists between the additional computational expense of generating k_i configurations for a single attempted reaction and overall phase space sampling. A simple approach was suggested for optimizing the value of k_i .

With minor modifications, the algorithm presented here could include orientational-bias techniques for polar molecules as well as biased sampling techniques for inserting long-chain molecules [25 and references therein].

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